

Distribution and Leaching of Methyl Iodide in Soil following Emulated Shank and Drip Application

Mingxin Guo,* Wei Zheng, Sharon K. Papiernik, and Scott R. Yates

ABSTRACT

Methyl iodide (MeI) is a promising alternative to methyl bromide in soil fumigation. The pest-control efficacy and ground water contamination risks of MeI as a fumigant are highly related to its gas-phase distribution and leaching after soil application. In this study, the distribution and leaching of MeI in soil following shank injection and subsurface drip application were investigated. Methyl iodide (200 kg ha⁻¹) was directly injected or drip-applied at a 20-cm depth into Arlington sandy loam (coarse-loamy, mixed, thermic Haplic Durixeralfs) columns (12-cm i.d., 70-cm height) tarped with virtually impermeable film. Concentration profiles of MeI in the soil air were monitored for 7 d. Methyl iodide diffused rapidly after soil application, and reached a 70-cm depth within 2 h. Relative to shank injection, drip application inhibited diffusion, resulting in significantly lower concentration profiles in the soil air. Seven days after MeI application, fumigated soil was uncapped, aerated for 7 d, and leached with water. Leaching of MeI was significant from the soil columns under both application methods, with concentrations of >10 µg L⁻¹ in the early leachate. The leaching was greater following shank injection than drip application, with an overall potential of 33 g ha⁻¹ for shank injection and 19 g ha⁻¹ for drip application. Persistent residues of MeI remaining in soils after leaching were 50 to 240 ng kg⁻¹, and the contents were slightly higher following shank injection than drip application. The results suggest that fumigation with MeI may pose a risk of ground water contamination in vulnerable areas.

METHYL IODIDE is a promising chemical alternative to methyl bromide (MeBr), which will be withdrawn from production and use in the United States by 2005 due to its potential to deplete stratospheric ozone. Laboratory and field studies have shown that MeI is equivalent to or more effective than MeBr in controlling nematodes, weeds, and other soil-borne pathogens (Becker et al., 1998; Waggoner et al., 2000). In the atmosphere, MeI degrades rapidly via photolysis, with a half-life of 4 to 8 d (Solomon et al., 1994), and it is not classified as an ozone-depleting compound.

Registration of MeI as a fumigant is expected soon (USEPA, 2004). Because MeI is a moderately toxic chemical and suspected carcinogen (Kutob and Plaa, 1962; International Agency for Research on Cancer, 1986), its emission to the atmosphere and leaching to ground

water after soil treatment are of great concern. To a certain extent, atmospheric emission and ground water leaching are related to its distribution and degradation after soil application. At 20°C, MeI has a vapor pressure of 398 mm Hg, and water solubility of 14 g L⁻¹. Gan and Yates (1996) studied the degradation and phase partition of MeI in soil, and found that in moist soil, degradation of MeI was mainly through chemical processes such as nucleophilic substitution reactions with H₂O (hydrolysis) or soil organic matter (methylation). They reported half-lives of MeI in mineral soil ranging from 11 to 43 d, a Henry's law constant (K_H) of 0.21 (21°C), and partition coefficients (K_d) on soil solids of 0.08 to 0.13 mL g⁻¹. Based on the results, the authors concluded that under normal conditions, the major portion (>55%) of MeI added to soil would remain in the aqueous phase, and the movement of MeI in soil would be dominated by gas-phase diffusion. In a field trial, Gan et al. (1997) observed that MeI migrated to a 180-cm depth from the surface within 72 h when the chemical was applied at a 30-cm depth in a sandy loam plot covered with 0.1-mm polyethylene film. Methyl iodide may be sufficiently persistent and diffusively mobile in soil to pose contamination risks to ground water in areas with shallow water tables.

In addition to the ground water quality ramifications, the distribution of MeI in soil also influences its pest-control efficacy. The pest-control efficacy of a fumigant is determined by its threshold exposure limits for pests, indicated by the concentration–time index ($CT = C^n t = k$, where C is the fumigant concentration, t is the exposure duration, the exponent n is the fumigant toxicity index, and k is a constant for pest mortality; Busvine, 1938). Most soil-borne pests are found in the plant root zone, which is generally the upper 30 cm of soil (Coyne, 1999). For shallow-rooted plants, limited downward diffusion of MeI, with higher concentrations maintained near the soil surface, may increase pest-control efficacy. Knowledge of gas-phase MeI distribution in soil after application will provide a basis for the prediction of pest-control efficacy and the selection of appropriate application dosages.

Fumigants are commonly shank-injected into field soils at various depths (i.e., 20–80 cm). To reduce emission loss and to achieve satisfactory pest-control efficacy, the soil surface is generally covered with polyethylene film for 7 to 14 d after fumigant application. Fumigants including 1,3-dichloropropene, chloropicrin, and methyl isothiocyanate can form persistent residues in soil that are resistant to volatilization and degradation (Guo et al., 2003a), and these residues may be released into the solution phase and leached through soil (Guo et al.,

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Abbreviations: MeI, methyl iodide; VIF, virtually impermeable film.

2003b). Retention of MeI in fumigated soils as persistent residues is unclear, and if formed, the leachability of these residues needs to be evaluated.

Recently, drip application of fumigants via irrigation systems has been proposed to reduce the chemical emissions from treated fields (Ajwa et al., 2002). Relative to shank injection, drip application alters diffusion and degradation patterns of fumigants in soil, and may influence leaching potential. To date, no data are available concerning the distribution of MeI and its leaching potential in soils following drip application. The objective of this study was to investigate the gas-phase distribution, leaching, and persistent residue retention of MeI in soils following shank injection and subsurface drip application.

MATERIALS AND METHODS

Soil Column Preparation

Arlington sandy loam soil was collected at a 0- to 20-cm depth from farmland in the University of California Agricultural Experiment Station in Riverside, CA. It has an organic C content of 9.2 g kg⁻¹, pH 7.2, and respective clay, silt, and sand content of 74, 180, and 746 g kg⁻¹. Stainless steel columns (70-cm height × 12-cm i.d.) were constructed as described in Gan et al. (2000). Gas-sampling ports (septa-sealed) were installed in the columns at 10-cm depth increments. A hole (5-mm i.d.) was drilled in the column bottom that was exposed to the atmosphere, intended to simulate the infinite downward diffusion of gases in field soils. A piece of stainless steel screen (0.2 mm) was placed at the bottom of each column, followed by a 3-mm sand layer (0.25–0.42 mm), to prevent fine soil particles from leaking through the bottom hole. Air-dried soil, sieved to <2 mm, was packed into the stainless steel columns to a depth of 67.0 cm. A total of 12.5 kg of air-dried soil was packed in each column to give a bulk density of 1.61 g cm⁻³, equivalent to that of the subsurface soil in the field. Two treatments with different fumigant application methods were included in this study: shank injection and drip application. For each treatment, duplicate columns were prepared. Two additional columns were prepared for soil moisture profile determination.

Solution (750 g of 5 mM CaCl₂ in water) was loaded to the column top to moisten the soil. This was to simulate the soil wetting procedure before bed preparation in field practices. The columns were then sealed with polyethylene film on the top, and settled for 60 d for equilibration. Final soil moisture contents from the column top to bottom were determined as 11.6% (3–30 cm), 9.2% (30–40 cm), 7.1% (40–50 cm), 3.1% (50–60 cm), and 2.0% (60–70 cm). The moisture profile was comparable with the field condition, which is typically 10% in the top 20 cm and 5% below 40 cm. The top 17 cm of soil in the columns was loosened by removing the soil, pulverizing it to <4 mm, and immediately replacing the pulverized soil to fully fill the column; the bulk density of the top 20 cm of soil was 1.29 g cm⁻³. This was to simulate the soil bedding operation in field practices. The columns were covered with virtually impermeable film (VIF) (Hytibar; Klerk's Plastic, Hoogstraten, Belgium) on the top to prevent moisture evaporation and chemical volatilization.

Soil Fumigation

The soil columns were set in a fume hood (21 ± 1°C). The MeI (98% purity; Chem Service, West Chester, PA) was

delivered to the column center through the injection port at a 20-cm depth. For shank injection, 100 µL of MeI were injected directly using a gas-tight syringe with a custom-made needle (7.5 cm long); for subsurface drip injection, 100 µL of MeI dissolved in 230 mL deionized water were applied at a 20-cm depth at a flow rate of 2.0 mL min⁻¹ using a peristaltic pump, and the delivery system was flushed twice with 20 mL of deionized water. To obtain a time-correspondent comparison, the shank injection was performed 10 min before the drip application was finished, which was considered as time zero. The fumigant application rate was 200 kg ha⁻¹ (176 lb acre⁻¹).

At predetermined times (2, 4, 6, 8, 10, 12, 24, 48, 72, 120, and 168 h after application), 250 µL of soil air were withdrawn through each sampling port in the columns, and transferred into a 9-mL headspace vial (clear borosilicate glass) that contained 0.1 g of anhydrous Na₂SO₄ (to absorb moisture). The vials were sealed immediately with aluminum covers and rubber septa, and stored at -76°C before chemical analysis. Preliminary tests showed that MeI was stable in clear glass vials under indoor fluorescent light (3 W m⁻²) for 72 h. Thus, photolysis of MeI during sample collection and analysis was assumed to be nil.

Fumigant Leaching

The soil columns were uncovered 7 d after the fumigant application, allowing open volatilization for another 7 d. Gas samples were collected again to test the residual MeI in the soil air. The columns were then leached with water (5 mM CaCl₂) to assess the leaching potential of residual MeI. Dilute CaCl₂ solution was loaded to the soil columns at 2 mL min⁻¹ with a peristaltic pump through an inlet port 2.5 cm from the top rim. Upon water addition, the top 20 cm of loosened soil collapsed approximately 5 cm. A constant head of 3 cm was maintained on the soil surface by pumping the excessively loaded water back to the reservoir through an outlet port 2 cm from the top rim. The saturated water conductivity (*K_s*) of the columns ranged from 0.24 to 0.58 cm h⁻¹, decreasing as the leaching process proceeded. The water flow rate from the bottom of the columns was 28 to 66 mL h⁻¹, higher initially and declining with time. Column leachate was collected in 500-mL flasks and the volume was recorded. At times when the flasks were full, 0.5 mL of leachate were withdrawn from the column bottoms using a gas-tight syringe, extracted with 3 mL of ethyl acetate and 3 g of anhydrous Na₂SO₄, and analyzed for MeI concentrations. This method has an extraction efficiency of 98.9 ± 11.5%.

The leaching process lasted for 19 d, until MeI in the leachate decreased to undetectable concentrations. After leaching, the columns remained in the fume hood for another 2 wk. Then soil samples were collected with an auger at every 10-cm depth increment from the column top rim. The soils were air-dried for 120 h, ground to pass a 2-mm sieve, and extracted with acetonitrile at 80°C to determine persistent MeI residues following the method described by Guo et al. (2003a).

Chemical Analysis

Concentrations of MeI in organic solvent extracts were analyzed with an HP 6890 gas chromatography (GC) system (Hewlett-Packard, Palo Alto, CA) equipped with an electron capture detector (ECD) and a DB-VRX capillary column (30-m length × 0.25-mm i.d. × 1.4-µm film thickness; J&W Scientific, Folsom, CA). The carrier gas (He) flow rate was 1.0 mL min⁻¹. The oven temperature program was as follows: held initially at 40°C for 6.5 min; then increased at 30°C min⁻¹

to 120°C, and held for 2 min. The retention time for MeI was 5.6 min, and the method detection limit was 13 ng L⁻¹.

Concentrations of gas-phase MeI in the headspace vials were analyzed on a Tekmar 7000 headspace autosampler (Full-Spectrum Analytics, Cincinnati, OH) in tandem with an HP5890 GC system equipped with an ECD and a DB-VRX capillary column. Conditions for the headspace autosampler were: equilibration temperature, 100°C; equilibration time, 2 min; and sample loop, 100 µL. The GC carrier gas (He) flow rate, inlet temperature, and detector temperature were set as 0.4 mL min⁻¹, 200°C, and 270°C, respectively. The oven temperature was held at initially 60°C for 1 min, and then increased at 10°C min⁻¹ to 150°C. The retention time for MeI under these conditions was 8.8 min, and the method detection limit was 11 ng L⁻¹.

RESULTS AND DISCUSSION

Gas-Phase Distribution of Methyl Iodide in Soil

In systems with varied moisture content, bulk density, and lower and upper boundary conditions such as the soil columns employed in the present experiments, diffusion and distribution of MeI is fairly complex and cannot be simply predicted by available mathematical models, and thus no modeling efforts were made to fit the experimental data. Measured concentration profiles of gas-phase MeI in soil columns in the 12 h after fumigant spiking are shown in Fig. 1. The highest concentration was typically present at the depth of fumigant placement (20 cm); away from the depth of placement, MeI decreased gradually with distance. The concentration peaks suggest that in VIF-tarped soil, MeI should be applied at soil depths of 20 cm to achieve best disinfestation effects in the upper 30 cm of soil. In practice, structural fractures may exist in fumigation beds, and cause rapid diffusion and uneven distribution of MeI in the

topsoil. Compaction of bed surfaces or tarping with VIF will minimize the preferential dispersion effect. Maximum gas-phase concentrations of MeI in the top 20 cm of soil occurred within 2 h following shank injection and within 4 h for drip application (Fig. 1). Even within 2 h, MeI in the soil air at a 70-cm depth became detectable (0.16 mg L⁻¹ for shank injection and 0.05 mg L⁻¹ for drip application). Evidently, MeI moved rapidly in soil after subsurface application. Methyl iodide has low molecular weight and high vapor pressure at room temperature, and its movement is dominated by gas-phase molecular diffusion (Gan et al., 1997), which is influenced by the soil's air-filled porosity. The top 20 cm of soil had lower bulk density (1.29 g cm⁻³) than the deeper soil (1.61 g cm⁻³), and diffusion of MeI in the former was much faster than in the latter, resulting in significantly higher concentrations of MeI in the soil air above the fumigant application depth (20 cm) than that below (Fig. 1). Plant pests abound in the root zone with a general concentration in the top 30 cm of soil (Coyne, 1999). Clearly, soil loosening practices such as tilling are necessary to enhance fumigant diffusion and disinfestation effects in the topsoil.

Relative to shank injection, drip application generated a much lower concentration profile of MeI in the soil air (Fig. 1). Under drip application the applied chemical was confined in the aqueous phase at the depth of placement. A high-water-content layer formed at 20 to 30 cm in the columns, and gas-phase diffusion of MeI was greatly limited. At 12 h, concentrations of MeI in the soil air were 5 to 12 mg L⁻¹ lower throughout the soil columns following drip application compared with shank injection (Fig. 1). The lower concentration profiles of MeI following drip application imply that at the

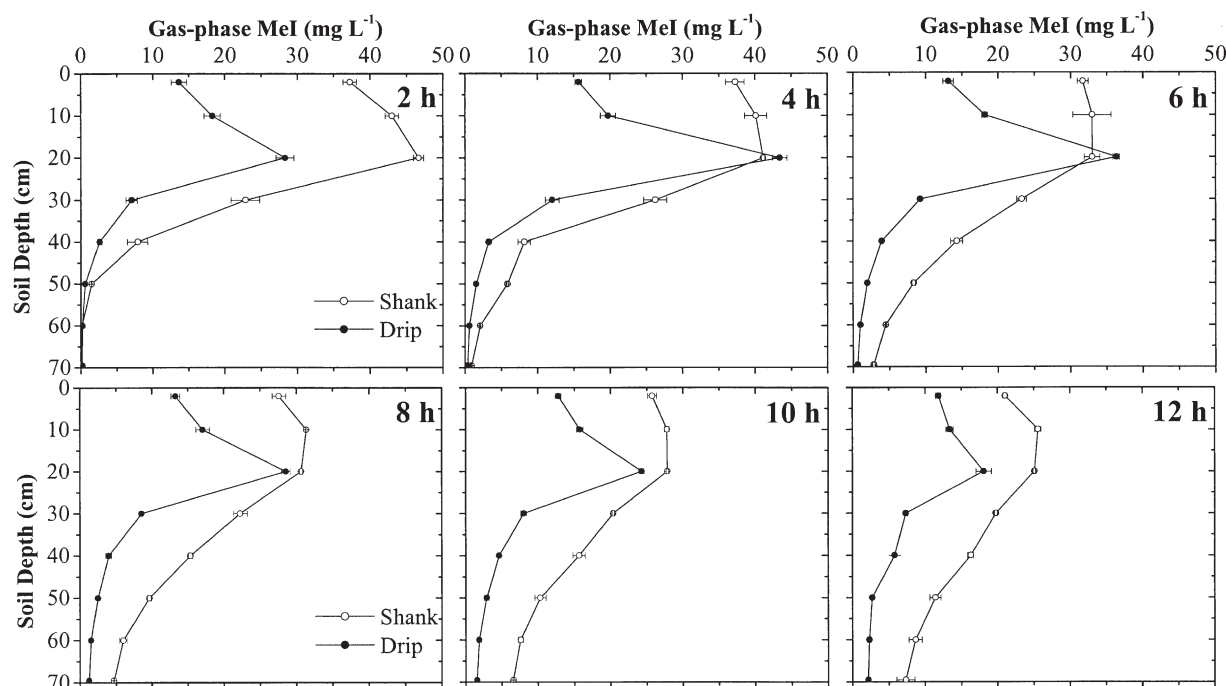


Fig. 1. Concentration profiles of gas-phase methyl iodide (MeI) in soil columns under shank injection and drip application 12 h after placement. Symbols represent the mean of duplicate measurements and error bars indicate the standard deviation.

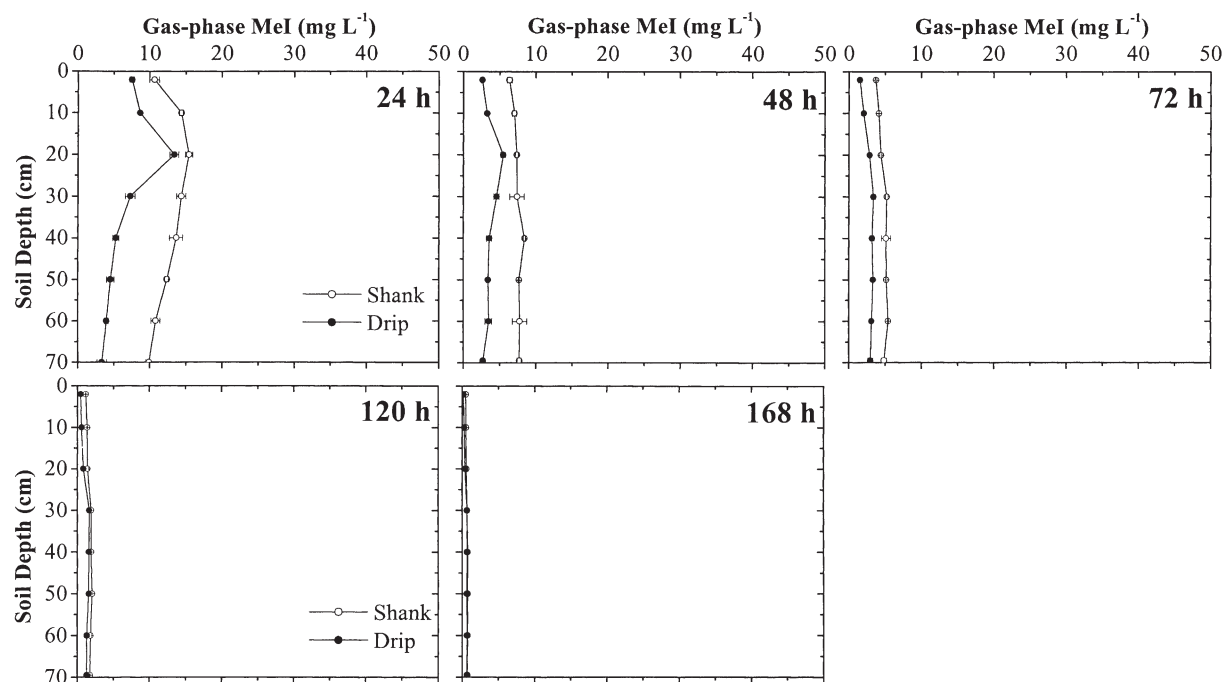


Fig. 2. Concentration profiles of gas-phase methyl iodide (MeI) in soil columns under shank injection and drip application between 24 and 168 h after placement. Symbols represent the mean of duplicate measurements and error bars indicate the standard deviation.

same fumigant application rates shank injection may be more effective in providing gas-phase pest control.

Gas-phase concentrations of MeI in the top 30 cm of soil started to decrease 4 h after application (Fig. 1). Because the soil surface was sealed with VIF, this is mainly a result of downward diffusion of the chemical. Accompanying the decrease in the upper layer was a gradual increase below a 40-cm depth. Within 12 h, MeI in the soil air at a 70-cm depth following shank injection and drip application approached 7.4 and 2.2 mg L⁻¹, respectively (Fig. 1). Gaseous MeI in the deep soils reached a maximum within 24 h, and the highest contents measured at a 70-cm depth were 9.9 mg L⁻¹ for shank injection and 3.4 mg L⁻¹ for drip application (Fig. 2). The rapid downward movement of MeI in soil poses ground water contamination risks, especially in field soils with preferential flow channels. When MeI was shank-injected at a 30-cm depth into a sandy loam field plot, it diffused more than 280 cm from the surface within 120 h (Gan et al., 1997). To protect ground water resources, the application rate of MeI should be strictly controlled.

The mean concentrations of gas-phase MeI at 24 h in the soil columns following shank injection and drip application were 12.7 and 6.8 mg L⁻¹, respectively. Assuming a phase equilibrium had been reached 24 h after MeI was spiked, a specific relationship was expected: C_g to C_l to C_s ratio = 2.1:10:1, where C_g (mg L⁻¹), C_l (mg L⁻¹), and C_s (mg kg⁻¹) are concentrations of MeI in the gaseous, aqueous, and sorbed phases, respectively, predicted from the K_H ($C_g/C_l = 0.21$) and K_d ($C_s/C_l = 0.1$ mL g⁻¹) at 21°C. The soil columns under shank injection contained air, water, and soil solids of 2550 mL, 949 mL, and 12.14 kg, respectively, and the columns under drip application, 2300 mL, 1199 mL, and 12.14 kg, respectively (calculated from soil moisture contents

and bulk densities, 21°C). Without consideration of volatilization and degradation losses, at 24 h the MeI (100 µL, about 223 mg) applied by shank injection would have a phase-equilibrium distribution of 19.8% in the gaseous phase, 35.2% in the aqueous phase, and 45.0% in the sorbed phase; the chemical placed by drip application would have a phase-equilibrium distribution of 16.7% in the gaseous phase, 41.4% in the aqueous phase, and 41.9% in the sorbed phase. The equilibrium concentrations of gas-phase MeI in the soil columns following shank injection and drip application at 24 h should have been 17.3 and 16.2 mg L⁻¹ respectively, much greater than the actual levels. Because degradation of MeI in moist soil is slow (half-life = 11–43 d), and volatilization through the VIF tarps was insignificant, the differences were mainly attributed to the emission loss through the hole in the column bottom (to simulate the infinite downward diffusion). Confinement of drip-applied MeI in the aqueous phase and the restriction of gas-phase diffusion by the high-water-content layer also contributed to the low concentrations of gaseous MeI in the soil columns following drip application. In fact, the bottom emission was so significant that the overall concentrations of gaseous MeI in the soil columns decreased more than 40% within 24 h, comparing the levels at 48 h to those at 24 h (Fig. 2). In field fumigation, infinite downward diffusion also causes drastic decreases of gas-phase MeI in upper layers. Gan et al. (1997) reported that the content of MeI in the soil air at a 100-cm depth from the surface decreased from 32 mg L⁻¹ at 24 h to 7 mg L⁻¹ at 72 h after applying the chemical at a 30-cm depth in a tarped sandy loam field.

The vertical distribution of gas-phase MeI in the soil columns was nearly uniform within 48 h, after which concentrations of MeI in the top 20 cm of soil air became

Table 1. Cumulative concentration–time products of gas-phase methyl iodide (MeI) in soils under shank injection and drip application.[†]

| Soil depth cm | Shank injection | Drip application |
|------------------|------------------------------------|------------------|
| | mg L ⁻¹ h ⁻¹ | |
| 2 | 811 (30.4) | 380.7 (25.1) |
| 10 | 934 (26.5) | 479 (11.5) |
| 20 | 973 (30.6) | 780 (31.4) |
| 30 | 872 (50.2) | 496 (33.0) |
| 40 | 774 (43.5) | 384 (25.1) |
| 50 | 686 (15.9) | 348 (17.0) |
| 60 | 630 (45.5) | 318 (21.9) |
| 70 | 586 (26.0) | 284 (22.7) |

[†] Values in parentheses are standard deviation of duplicate measurements.

appreciably lower than that below 20 cm (Fig. 2). Seven days (168 h) after application, MeI in the soil air was <0.7 mg L⁻¹, and the concentration profiles in both application treatments converged (Fig. 2). To prevent air pollution from MeI fumigation, a VIF soil cover and a longer tarping time (i.e., 10 d) may be necessary.

Concentration–Time Products of Methyl Iodide in Soil

The pest-control efficacy of a fumigant is determined by its vapor concentration and the exposure duration of target pests, which can be described by the model $C^n t = k$ (Busvine, 1938). Generally it can be assumed that exposure duration is equally important as concentration, and thus $n = 1$. To indicate the potential pest-control effects of MeI under different application methods, the cumulative concentration–time products (CT = $\int C_i dt$) of MeI in soil at different depths were estimated by $CT = \sum C_i T$, where C_i is the gas-phase concentration of MeI measured at time t , and T is the time elapsed from the last measurement. Calculated CTs are listed in Table 1. The shank injection had remarkably higher gas-phase CTs (580–970 mg L⁻¹ h) than the drip application (280–780 mg L⁻¹ h); values were approximately doubled except at the depth of placement (20 cm). The CT index of MeI for pests is not known. By exposing a variety of insects including wheat aphid, vine mealybug, red scale, grain moths, and mites to 96 mg L⁻¹ of MeI in glass jars, Waggoner et al. (2000) reported that 92 to 100% of the test pests were killed within 2 h. If the CT index was set as 384 mg L⁻¹ h (double of 96 mg L⁻¹ × 2 h), either shank injection or drip application of MeI at 200 kg ha⁻¹ would generate satisfactory pest-control efficacy. The first 72 h after application represented more than 85% of the cumulative CTs in the upper 40-cm soil layers following shank injection and >70% following drip application, respectively. Predicting from the cumulative CT values, satisfactory pest control may be achieved when MeI is shank-applied at reduced rates (i.e., 100 kg ha⁻¹) to soils tarped with VIF.

Residual Gas-Phase Methyl Iodide in Soil

Concentration profiles of residual gas-phase MeI in soil 7 d after removal of the plastic tarp (14 d after

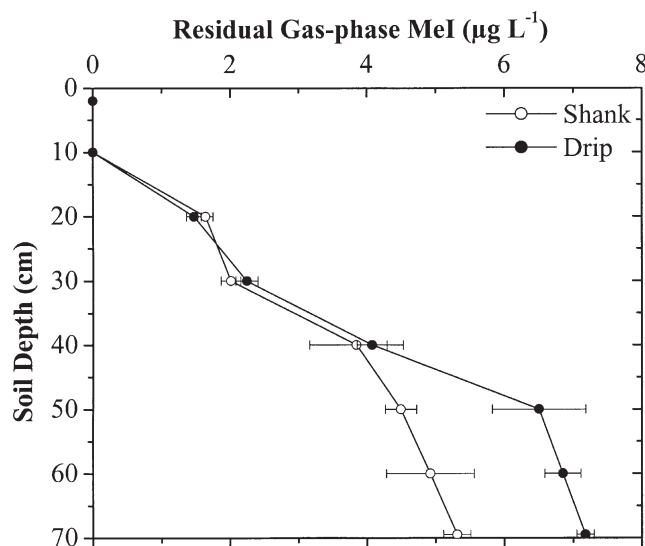


Fig. 3. Residual gas-phase methyl iodide (MeI) in the soil air after 7 d of volatilization in the open atmosphere. Symbols represent the mean of duplicate measurements and error bars indicate the standard deviation.

fumigant application) are illustrated in Fig. 3. Most of the MeI in the soil air (about 0.7 mg L⁻¹ on removal of the tarp; Fig. 2) had dissipated. At 2- and 10-cm depths, no gaseous MeI residues were detected. At the depth of placement (20 cm), MeI in the soil air was <1.6 µg L⁻¹. The residual gas-phase MeI increased with soil depth, suggesting that in open systems volatilization outweighed other processes such as degradation in MeI dissipation.

The top 40 cm of soils in the columns following shank injection and drip application had similar contents of residual gaseous MeI. Below the 40-cm depth, however, the residual contents were significantly greater in columns following drip application than following shank injection (Fig. 3). This was evidently caused by the higher water content that impeded the gas-phase diffusion of MeI vapor under drip application. Even so, the gas-phase concentration of MeI at the 70-cm depth in columns following drip application was 7.2 µg L⁻¹, one hundredth of that on the tarp removal. From the mass balance viewpoint, it is inferred that a significant portion of MeI in the water phase following drip application had volatilized to the atmosphere after surface tarp removal. The low residual MeI indicated that the fumigated soils were probably safe for planting. In columns following shank injection, soils below the 40-cm depth had residual MeI of about 23 µg L⁻¹ in the aqueous phase and 2.3 µg kg⁻¹ in the sorbed phases, estimated from K_H and K_d of the chemical. In columns following drip application, the contents were around 31 µg L⁻¹ and 3.1 µg kg⁻¹, respectively. The residual MeI was subject to leaching.

Leaching of Residual Methyl Iodide in Soil

Seven days after the tarp removal, the soil columns were leached with dilute CaCl₂ solution. Upon water addition, the loosened top 20 cm of soil collapsed immediately due to the lower bulk density, and the columns shrank about 5 cm. A 3-cm constant water head was

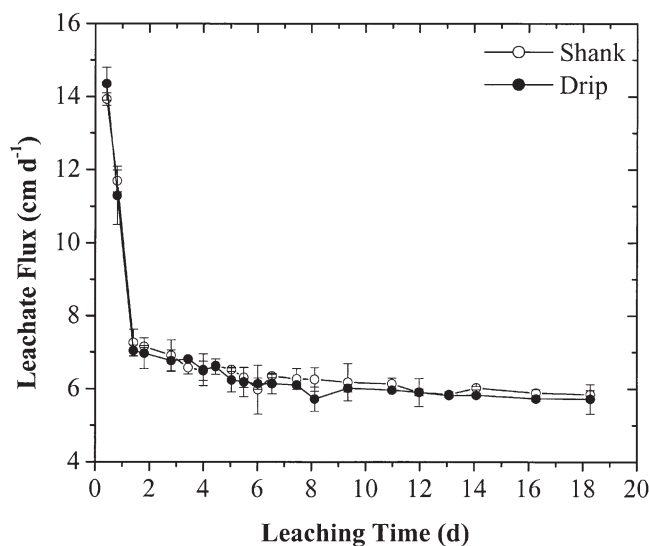


Fig. 4. Leachate fluxes from soil columns under shank injection and drip application. Symbols represent the mean of duplicate measurements and error bars indicate the standard deviation.

maintained on the soil surface, and water percolated through soil by gravity. Initially, water moved at a high flow rate, and the leachate flux was approximately 14.0 cm d^{-1} (Fig. 4). The leachate flux decreased rapidly to about 7.0 cm d^{-1} within the initial 36 h of the leaching process, a result of soil compaction by the added water and pore clogging by clay particles. The leaching process lasted for 19 d. The flux decreased to $<5.8 \text{ cm d}^{-1}$ in the late stage, and $>4 \text{ d}$ were required to collect one pore volume (2832.5 cm^3) of leachate.

Concentrations of MeI in the leachates are presented in Fig. 5. The leaching curves were characterized by an initial high concentration, followed by a rapid decrease in the first pore volume and a long tailing to four pore volumes. The early leachates from the columns following shank injection and drip application contained 15.0 and $9.9 \mu\text{g L}^{-1}$ of MeI, respectively, much greater than the gaseous residual contents in soil before the water leaching. Although water quality standards for MeI have not been established, low tolerances are generally established for toxic organic chemicals, including fumigants, in drinking water. For example, the California Environmental Protection Agency (CAEPA) has developed a public health goal for the fumigant 1,3-dichloropropene in drinking water as $0.2 \mu\text{g L}^{-1}$ (California Environmental Protection Agency, 1999). Fumigant concentrations resulting in ecotoxicological effects are extremely low, mostly $<0.1 \mu\text{g L}^{-1}$ (Notenboom et al., 1999). Therefore, the leaching of MeI from the treated soil columns was significant, and cannot be ignored. It was unexpected that leachate from the columns following shank injection had significantly higher MeI concentrations than that from the columns following drip injection (Fig. 5), because residual gaseous MeI was lower in the former than the latter (Fig. 3).

Sorption of fumigants on soil is quite complex and cannot be adequately described by K_d . Studies have shown that sorption of fumigants on soil decreases as the moisture content increases (Tamagawa et al., 1985). Drip appli-

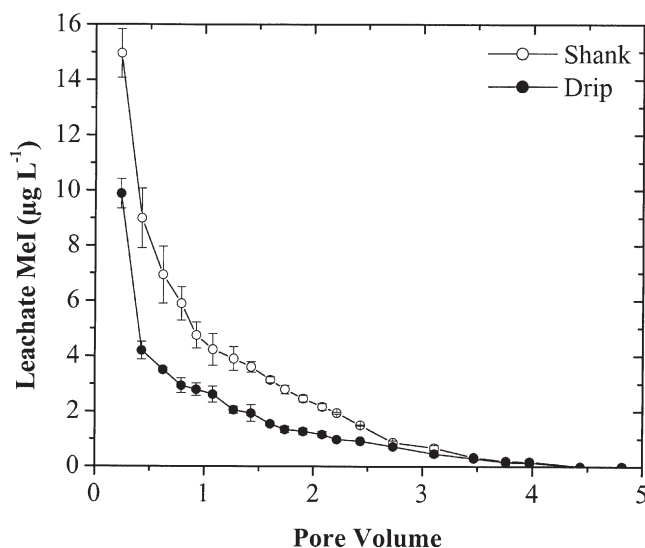


Fig. 5. Concentrations of methyl iodide (MeI) in leachates from soil columns under shank injection and drip application. Symbols represent the mean of duplicate measurements and error bars indicate the standard deviation.

cation may have reduced sorption of MeI to soil through elevating the moisture content. Furthermore, sorption of fumigants to soil is not simply a phase equilibrium between the gaseous, aqueous, and sorbed phases. Substantial amounts of fumigants may still remain in the soil matrix even if the contents of the chemicals in the aqueous and gaseous phases become undetectable (Guo et al., 2003a). This portion of fumigants is believed to be entrapped in soil intra-aggregate micropores instead of being attached on particle surfaces. Unlike the fractions adsorbed on particles surfaces, the entrapped fumigants are resistant to volatilization and biodegradation. Nevertheless, the fraction of fumigants entrapped in soil micropores is susceptible to leaching (Guo et al., 2003b). Diffusion of fumigants into soil micropores is via thermal molecular motion and driven by the concentration gradient, so the amount of fumigants entrapped in soil micropores correlates to gas-phase concentrations of the chemicals during the fumigation period. Laboratory soil incubation tests revealed that persistent residues of the fumigants 1,3-dichloropropene, chloropicrin, and methyl isothiocyanate increased as the application rate increased (Guo et al., 2003a). In this study, the higher gas-phase concentrations MeI in the soil columns following shank injection may have resulted in greater entrapment of the chemical in soil solids, which was leached out by water percolating into the micropores. Cumulatively, $37.5 \pm 3.3 \mu\text{g}$ and $21.4 \pm 1.5 \mu\text{g}$ of MeI were leached out of the columns following shank injection and drip application, respectively. Extrapolating from these soil column results, leached residues are estimated as $32.8 \pm 2.9 \text{ g ha}^{-1}$ and $18.7 \pm 1.3 \text{ g ha}^{-1}$ for fields treated with MeI by shank and subsurface drip application at a rate of 200 kg ha^{-1} . Although the leached MeI totaled $<0.02\%$ of the applied amount, leaching should be considered in view of ground water protection.

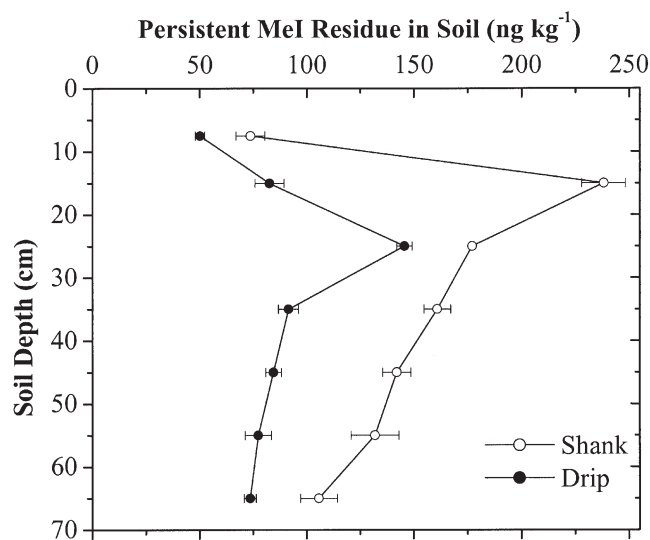


Fig. 6. Persistent residues of methyl iodide (MeI) remaining in soils after water leaching. Symbols represent the mean of duplicate measurements and error bars indicate the standard deviation.

Persistent Methyl Iodide Residues in Soil

Contents of MeI remaining in soil after leaching are demonstrated in Fig. 6. Despite the low contents (50–240 ng kg⁻¹), it is evident that a small portion of the applied MeI was retained as persistent residues. In both application treatments, the topsoil (0–10 cm) had the lowest contents of persistent MeI residues, probably due to the dispersion of soil aggregates on long-term water flooding. The persistent residues peaked at the depth of placement (10–20 cm for shank application and 20–30 cm for subsurface drip application), and decreased in deeper soils (Fig. 6), similar to the initial distribution of gas-phase MeI in the soil columns (Fig. 1). At the same depth, soil columns following shank injection had a consistently greater concentration of persistent MeI residues than columns following drip injection (Fig. 6), consistent with the concentration profiles of gas-phase MeI during the fumigation period (Fig. 1).

Leaching of fumigant residues entrapped in soil micropores is determined by percolation of water into soil aggregates. Under normal conditions, a portion of micropores are not available to water molecules due to tortuosity. In a column study, Guo et al. (2003b) observed that 6 to 51% of persistent 1,3-dichloropropene, chloropicrin, and methyl isothiocyanate residues remained in soils after leaching with 10 pore volumes of water. The un-leachable fumigant residues are inactive, and may not be considered in soil remediation. However, under extreme conditions such as repeated wet-dry and freeze-thaw cycles, soil aggregates may break down and retained fumigant residues may be released. The effect of wet-dry and freeze-thaw cycles on the release of persistent pesticide residues needs investigation.

CONCLUSIONS

Gas-phase distribution and leaching of MeI in soil following shank injection and drip application were in-

vestigated with laboratory column techniques. When applied at a 20-cm depth to VIF-tarped soil, MeI diffused rapidly in moist soils, and reached a 70-cm depth within 2 h, posing contamination risks to shallow ground water. The gaseous diffusion flux was controlled by soil bulk density and moisture content. The highest concentration of MeI in the soil air was present at the depth of placement, and shank injection resulted in significantly higher gas-phase concentration profiles than drip application. Residual vapor MeI was higher in soils following drip application than following shank injection 7 d after the tarp removal, but gas-phase concentrations were <7.1 µg L⁻¹ for both application methods. Leaching of MeI was significant from soil columns under both application methods, with concentrations of the chemical in early leachate being >10 µg L⁻¹. Leaching of MeI was greater from the columns following shank injection than following drip application, and the extent was estimated as 33 g ha⁻¹ for the former and 19 g ha⁻¹ for the latter. A slight amount of MeI remained in soil as persistent residues after leaching, and the content was higher in soils following shank injection than following drip application. Relative to shank injection, drip application reduces diffusion, leaching, and retention of persistent residues of MeI in soil.

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